DYNAMICS SIMULATION OF VINYL CHLORIDE MONOMER (VCM) REACTOR USING ASPEN HYSYS

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Thesis submitted in fulfillment of the requirements

for the award of the degree of

Bachelor of Chemical Engineering

Faculty of Chemical Engineering & Natural Resources

UNIVERSITI MALAYSIA PAHANG

FEBRUARY 2013

ABSTRACT

The purpose of this research is to observe the dynamics simulation of Vinyl Chloride Monomer (VCM) process particularly in reaction section. The simulation is conducting by Aspen Hysys software by applied some steps. To develop dynamics simulation, the first step is developing steady state mode. Once the steady state simulation have completed, then sizing and installing the controller should be done. The third step is tuning of the controller. The characteristics of the reaction process can be investigated by changing of a raw materials flow rate. The result shows that the transient responses of the VCM reactor are inverse response process. The outcome result of this research is the oxychlorination reactor section of vinyl chloride monomer can be develop by using dynamics simulation as the monitoring process if any disturbances occur after the parameter is changed in process meanwhile the environment and safety of human secured from any pollution and dangerous incident. Apart from that, this study can become guidance to VCM industry to improve process performance. The significant of the study is improving knowledge of the characteristic of VCM process in reactor section by simulating process using dynamics simulation. Another significant is commercialization of dynamics simulation to VCM industries that bring 1001 benefit to industries.

ABSTRAK

Tujuan kajian in adalah untuk memerhati process simulasi dinamik vinil kloride monomer terutamanya di dalam seksyen reaksi. Simulasi dijalankan oleh perisisan Aspen Hysys dengan mengunakan beberapa langkah. Untuk membangunkan simulasi dinamik, langkah pertama adalah membangunkan mod keadaan stabil. Setelah simulasi keadaan stabil telah selesai, maka saiz dan memasang kontroler perlu dilakukan. Langkah ketiga adalah mengawal kontroler. Ciri-ciri proses tindak balas boleh disiasat oleh perubahan kadar aliran bahan-bahan mentah. Hasilnya menunjukkan bahawa tindak balas sementara reaktor VCM adalah proses tindak balas songsang. Keputusan hasil kajian ini adalah seksyen oxychlorination reaktor vinil klorida monomer boleh dibangunkan dengan menggunakan simulasi dinamik sebagai proses pemantauan jika sebarang gangguan berlaku selepas parameter berubah dalam proses. Sementara itu, alam sekitar dan keselamatan manusia dipelihara daripada sebarang pencemaran dan kejadian berbahaya. Selain daripada itu, kajian ini boleh menjadi panduan kepada industri VCM untuk meningkatkan prestasi proses. Signifikan kajian meningkatkan pengetahuan tentang ciri-ciri proses VCM dalam seksyen reaktor oleh simulasi proses menggunakan simulasi dinamik. Satu lagi kesan yang ketara adalah pengkomersilan simulasi dinamik kepada industri VCM yang membawa 1001 manfaat kepada industri.

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LIST OF ABBREVIATIONS

PVC	Poly Vinyl Monomer
VCM	Vinly Chloride Monomer
SP	SetPoint
OP	Output Signal
PV	Process Variables
EDC	Ethylene dichloride/ 1,2-Dichloroethane
OSHA	Health and safety regulations
PPM	Part per Million
HCI	Hydrogen Chloride

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND OF RESEARCH

Vinyl chloride is the organic chloride that most important in industrial chemical used to produce the polymer polyvinyl chloride (PVC). The chemical compound 1,2-dichloroethane or ethylene dichloride (EDC), is a chlorinated hydrocarbon, mainly used to produce vinyl chloride monomer (VCM,) EDC is a colourless liquid with a chloroform-like odour. VCM and EDC are very harmful substances where both this substances is toxic and flammable, then the manufacture of VCM and EDC should concerns regarding to hazard, safety and pollution. The required development the software of chemical process gives significant impact in chemical process simulation. With the small number of VCM industry that using the simulation on their process, this research will bring the opportunity to industry where dynamic simulation can be one tool to reduce plant design time by allows designer to quickly test various plant configurations without effect the society and environment. A process simulation also displays significant features and characteristics of the system which one wishes to study, predict, modify or control. It also represents some dynamic system be use to gain important information when the costs, risks or logistics of manipulating the real system in plant are prohibited. Therefore this research is important to industry prove to society that the modern VCM industry is more safety and cleanest.

1.2 PROBLEM STATEMENT

The increasing of polyvinyl chloride (PVC) gives impact to increase of production of vinyl chloride monomer (VCM). VCM is produced from the exothermic reaction. The raw materials of production VCM is ethylene, chlorine and oxygen where all the material is 100% pure. As an exothermic reaction, it will give the biggest problem that is runaway reaction in process. Besides that two from raw material which ethylene and oxygen are flammable and toxicity substance. Thus, a dynamics simulation representation consistent with the actual plant needs to be developed as a benchmark for chemical process engineers to improve the performance of the process. Then the hazard effect to people, environment and properties can be avoided.

1.3 RESEARCH OBJECTIVE

The objective of this research is;

1. To develop dynamics simulation of VCM process (reaction section) using Aspen Hysys software.
2. To provide troubleshooting guideline before applied into actual plant.

1.4 RESEARCH QUESTION

The research question that will obtain from this research is:

1. How to develop dynamics simulation of VCM process (reaction section).
2. Can dynamic simulation of VCM process provide a benchmark to chemical engineer to improve the performance of the process?
3. Can dynamics simulation provided the troubleshooting occur in VCM process?

1.5 SCOPE OF STUDY

The scope of the researches is the dynamics behavior on VCM in reactor section that require specific operating procedure to ensure the reaction process is stable. In addition for scope of software for dynamic simulation is ASPEN HYSYS.

1.6 EXPECTED OUTCOME

From the study, the vinyl chloride monomer (VCM) can be demonstrated using dynamics simulation. The result of this study can become guidance to VCM industry to improve process performance and safety.

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1.7 SIGNIFICANCE OF STUDY

The significant of the study is improving knowledge of the characteristic of VCM process by using dynamics simulation. Another significant is commercialization of dynamics simulation to VCM industries.

1.8 CONCLUSION

This study is highly beneficial and most helpful research for industries to analysis any question or problems that related to abnormal of process production VCM in reactor section using dynamics simulation to obtain quality and quantities product without effect on environment, property, human safety and organization cost. Investigate ways to support the integration of representation, guidance, simulation and execution capabilities for models of software processes.

CHAPTER 2

LITERATURE REVIEW

2.1 INTRODUCTION

The purpose of this chapter is to provide a literature review of past research effort such as journals or articles related to reactor section and dynamics simulation analysis for production of vinyl chloride monomer (VCM). Moreover, review of other relevant research studies are made to provide more information in order to understand more on this research. Health and safety regulations (OSHA) require the monitoring of concentrations of hazard species in all facilities where VCM is produced or used. The time for person can be in environment that exposed to less than 1 ppm is over 8 hours and cant exceeding 15 minute for no more than 5 ppm environment. Exposures to more than 100 ppm can bring to dangerous disease to person. The characteristic of VCM is flammable to heat, flame and oxidizing agent based on fire triangle. The use of stabilizers prevents polymerization during processing and storage (Alexandre 2008). Dynamics simulation is one tool that plays a significant role in improving product quality, plant efficiency, and safety. The respond that come from the dynamics simulation are useful tool that can be applied to all tasks of process operation to predict the behavior of specific unit or process. Software modularity, user friendly interfaces and computing power has increasingly opened up new opportunities for the application of advanced mathematical models in process operations. In new global competition to produce good quality of VCM, organization need to accelerate process engineering design, reduce capital costs and optimize the various process operations (Kellner et al, 1999).

2.2 VINYL CHLORIDE MONOMER (VCM) PROCESS

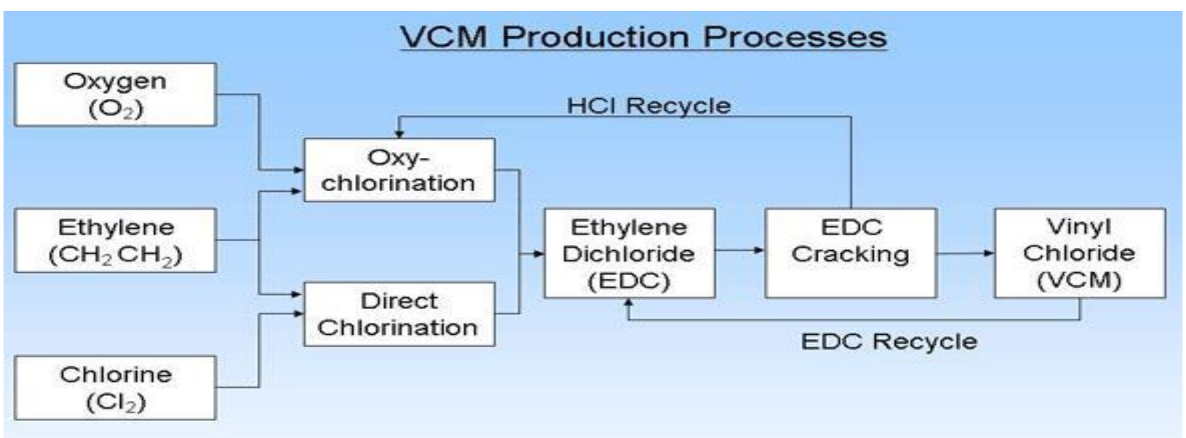

Figure 2.1: Block Diagram of VCM Process

Based on the figure 2.1, Vinyl chloride monomer (VCM) or (CH_2=CHCL) process is involved 3 sections which reaction section, separation section and purification section. For reaction section, the process that involved is recovery of HCl with oxychlorination process and direct chlorination process. In separation process is thermal cracking (pyrolysis) process and purification section is VCM purification. For this research only oxychlorination process in reaction section been focus where 85% of amount 1,2 – ethylene dichloride (EDC) produce from this process (Alexandre, et,al, 2008). The three main steps process are explained briefly below:

- Direct chlorination of ethylene to 1,2 - ethylenedichloride (EDC):
  - $\mathbf{C_2H_4 + Cl_2 \rightarrow C_2H_4Cl_2 + 218\ kJ/mol}$
- Thermal cracking (pyrolysis) of EDC to VCM:
  - $\mathbf{C_2H_4Cl_2 \rightarrow C_2H_3Cl + HCl - 71 kJ/mol}$
- Recovery of HCl and oxychlorination of ethylene to EDC:
  - $\mathbf{C_2H_4 + 2HCl + 0.5O_2 \rightarrow C_2H_4Cl_2 + H_2O + 238\ kJ/mol}$

Hence, an ideal balanced process can be described by the overall equation:

$$\mathbf{C_2H_4 + 0.5Cl_2 + 0.25O_2 \rightarrow C_2H_3Cl + 0.5H_2O + 192.5 kJ/mol}$$

2.2.1 Oxychorination process.

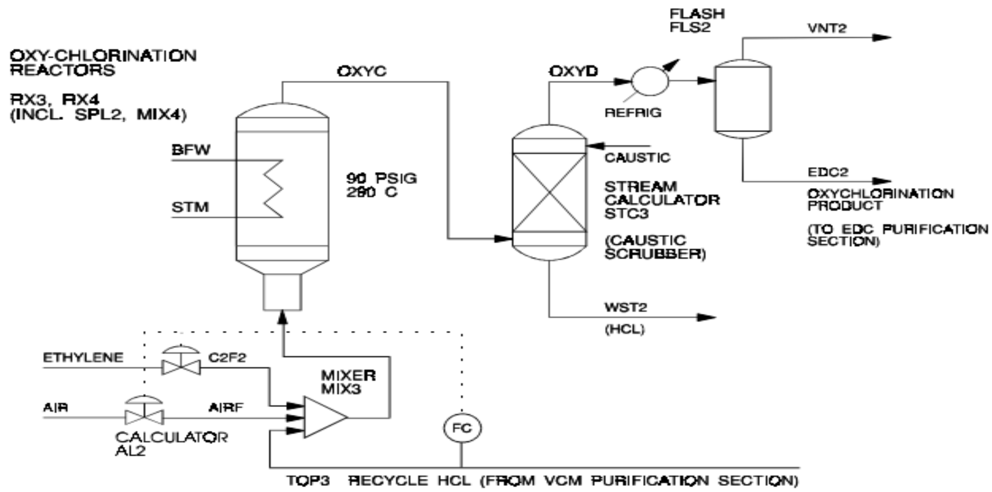

Figure 2.2: Process Flow Diagram For Oxychorination Process

The term of oxychlorination describes a process whereby chlorination usually of hydrocarbon is achieved with hydrogen chloride and oxygen in the present of catalyst (Magistro et al, 1968). In production Vinyl Chloride Monomer (VCM), oxychlorination is one process in production of where in this process the ethylene, dry HCI and air or pure oxygen is react in a heterogeneous catalytic reaction to form EDC and water. The reaction such as:

$$\mathbf{C_2H_4 + 2\,HCl + \tfrac{1}{2}O_2 \rightarrow C_2H_4Cl_2 + H_2O}$$

The oxychlorination of ethylene to EDC and water is conducted in the gas phase at specify parameter such temperature in range between 200-300° C and pressure between 2-4 bar in fixed - bed reactors or fluid - bed reactors. The fluid - bed technique offers more intensive heat transfer, prevents the occurrence of hot spots and allows more efficient catalyst regeneration. Function of fluid bed reactor is by improve contact two phases in a chemical process and is used to store heat in chemical process. The excellent distribution in fixed-bed makes it possible to maintain a constant temperature to ensure low by-product formation and to achieve optimum process control. The reaction gas passes a filter unit in which the catalyst fines are separated from the gas.

From this reaction the conversion of EDC can achieved with selectivity between 91 – 96% from the ethylene conversion of 93 – 97%. An increase in by-product formation is observed with increasing reactor temperature. The oxychlorination reaction is exothermic reaction where heat capacity is -238 kJ/mol EDC made) and requires heat removal for temperature control, which is essential for efficient production of EDC. Higher reactor temperatures lead to more by-products, mainly through increased ethylene oxidation to carbon oxides and increased EDC cracking yield VCM and cracking steps lead progressively to by-products with higher levels of chlorine substitution. The $CuCl_2$ serves as catalyst often contain activators and stabilizers such as chlorides of the rare earths and alkali metals. Under the reaction condition is no free chlorine (Wakiyama, 1971). Catalyst also deactivate if the temperature is high more than 300°C though the sublimation of $CuCl_2$ increased. The process flow diagram is like in figure 2.1. Ethylene, oxygen and recycle HCl will mix first in mixer before entering the reactor section. The product from reactor section will enter caustic scrubbing tower where unreacted HCl is removed. The vapor then passes to a refrigerated condensation system to recover EDC and water. The product steam is cooled and flashed to remove all non condensable mainly nitrogen and unreacted oxygen at top product and EDC at bottom product before the EDC flow to purification section.

Some key impurities are listed below: 1,1,2 - trichloroethane (TCE), chloral (CCl 3 - CHO), trichloroethylene (TRI), 1,1 - and 1,2 - dichloroethylenes, ethyl chloride, chloro - methanes (methyl -chloride, methylen - chloride, chloroform), as well as polychlorinated high – boiling components (Alexandre et al, 2008). In particular, chloral needs to be removed immediately after reaction by washing because of its tendency to polymerization. The formation of TRI is undesired, because its removal by distillation is very difficult. In fact, TRI and EDC form a low - boiling point azeotrope very close to EDC. The formation of TRI in the oxychlorination reactor is due to the acetylene entrained with the HCl byproduct from cracking. Secondary reactions manifest, as explained next. An amount of ethylene is lost by combustion at higher temperature:

$$\mathbf{C_2H_4 + O_2 = Cl_2 + H_2O}$$

$$\mathbf{HCl + 0.5O_2 = Cl_2 + H_2O}$$

Chlorine is involved further in radical reactions producing many chlorinated species. At higher temperature even the C – C bond in chlorinated products can break, forming chloromethanes (Alexandre et al, 2008). All these reactions lead finally to a wide spectrum of impurities. Stoichiometric equations are given below and may be used for material - balance purposes, although the true reaction mechanism is much more complex:

$$\mathbf{C_2H_4C_{l2} + Cl_2 = C_2H_3Cl_3\ (TCE) + HCl}$$

$$\mathbf{C_2H_2 + 2Cl_2 = C_2HCl_3\ (TRI) + HCl}$$

$$\mathbf{C_2H_4 + 2Cl_2 + O_2 = Cl_3C{-}CHO(CLAL) + HCl + H_2O}$$

$$\mathbf{C_2H_6 + Cl_2 = C_2H_5Cl\ (ETCL) + HCl}$$

$$\mathbf{C_2H_4 + 2Cl_2 = C_2H_3Cl_3\ (TEC) + HCl}$$

$$\mathbf{C_2H_2 + 3Cl_2 = 2CHCl_3\ (TCM)}$$

$$\mathbf{C_2H_4 + 4Cl_2 + O_2 = 2CCl_4 + 2H_2O}$$

$$\mathbf{C2H_4 + Cl_2 = C_2H_2Cl_2\ (DCE=) + 2HCl}$$

$$\mathbf{2C_2H_4Cl_2 = C_4H_8Cl_2\ (heavies) + HCl}$$

2.3 DYNAMIC SIMULATION

In industry of VCM, redesign and optimization of existing process is required to produce the quality product. To overcome the problem, dynamic simulation is needed for all engineers as well as by other operational groups is highly desirable. By applied the dynamics simulation into VCM production, the whole plant can be described into dynamics model for purpose to address a variety of abnormal issues from the process, and to supporting process improvements,

In many cases, simulation is an aid to decision making. It also helps in risk reduction and helps management at the strategic, tactical and operational levels. There has a reason for engineer to use the dynamics simulation into real plant. First purpose is control and operational management. For these advantages simulation can also provide effective support for managerial control and operational management. Simulation can facilitate project tracking and oversight because key project parameters such actual status and progress on the work product, raw material consumption and etc can be monitored and compared against planned values computed by the simulation. This helps personnel determine when possible corrective action may be needed. The major activity of support operational decisions such coding and integration testing can be commencing by using simulation. Evaluating current project status using timely project data and employ simulation to predict the possible outcome if proposed actions such commence integration testing can be taken or delay can be due by personnel (Kellner et al, 1999). Another purpose is process improvement and technology adoption from organization plant in a variety of ways. In process improvement settings, organizations plants are often faced with many suggested improvements. Advantage of dynamics simulation is simulation can provide specific process improvement decisions such as go/no go on any specific proposal, or prioritization of multiple proposals by forecasting the impact of a potential process change before putting it into actual practice in the organization.

Finally, the advantage by using dynamics simulation in VCM process is training through involved in simulations can help people to accept the uncertainty of their initial prediction about the results of given actions in process. There has two type of person where one has abilities to predict from data and one do not possess good skills or inherent abilities to predict the behavior of systems with complex feedback loops and/or uncertainties as are present in software processes. Overall, active participation in a good mix of simulations can provide learning opportunities to personnel that could compare real world experience that only be gained through years in industry (Kellner et al, 1999). The developed software tools support the application of model-based approaches to the design, operation, optimization, and control of polymerization processes. Ideally, such a model can predict the steady-state and dynamic behavior of a process over a wide range of operating conditions to an acceptable degree of accuracy (Krallis et al, 2010).

For the reactor in Aspen Hysys, all of the reactor operations share the same basic property view. The primary differences are the functions of the reaction type (conversion, kinetic, equilibrium, and heterogeneous catalytic or simple rate) associated with each reactor. As opposed to a separator or general reactor with an attached reaction set, specific reactor operations may only support one particular reaction type. For instance, a conversion reactor will only function properly with conversion reactions attached. If you try to attach equilibrium or a kinetic reaction to a conversion reactor, an error message will appear. The gibbs reactor is unique in that it can function with or without a reaction set. Conversion reactors can be used to quickly calculate reaction products. The conversion of a specified reactant is described by an equation which can be a function of temperature. A conversion reactor might be used in place of a plug flow reactor with multiple reactions inside a recycle loop in order to save time. The actual plug flow reactor calculations would be done once the recycle is converged and conditions are more finalized. Another situation where conversion reactors are useful is when product yields are known but detailed kinetics may not be available. Many refinery reactors, including hydro treating, alkylation, catalytic cracking, coking, and others can be modeled with conversion reactors. Another reason for the conversion reactor been used in this simulation is because conversion reactor is a basic for the fluid bed reactor.